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14. ABSTRACT JHU/APL's Polymer Claw is a pressure-activated underwater adhesive that bonds instantly to biofouled surfaces in a single step. The key to this technology is the use of pressure sensitive microcapsules, which release reactive amine crosslinkers into an adhesive putty when pressed against the surface. The amine reacts with the sticky, isocyanate putty to form a tough polyurea. The catalyzed isocyanates likewise bond with alcohols, amines, acids, or oxides on the surface. This technology addresses the issue of biofouling through an abrasive metal brush coated with a caustic gel. Activated by water, the caustic removes plant and animal matter before the adhesive even makes contact with the surface. Pressure from the adhesive putty flattens the metal bristles and displaces the gel to make way for the adhesive. The entire system will be sealed in disposable packaging for safe storage and transport. This aggressive approach meets the Navy's requirements for speed, robust performance in all conditions, and no special training.				
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POLYMER CLAW: INSTANT UNDERWATER ADHESIVE

Progress Report #6

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TABLE OF CONTENTS

<u>1</u>	<u>SUMMARY</u>	<u>3</u>
<u>2</u>	<u>PROJECT GOALS AND OBJECTIVES</u>	<u>3</u>
<u>3</u>	<u>KEY ACCOMPLISHMENTS</u>	<u>3</u>
3.1	ABRASIVE BRUSH FABRICATION	3
3.2	CAUSTIC CLEANING AGENT RHEOLOGY	3
3.3	PRESSURE-ACTIVATED ADHESIVE	5
3.3.1	PROCESSING IMPROVEMENTS	5
3.3.2	MICROCAPSULE DIAMETER	5
3.3.3	MICROCAPSULE/RESIN RATIO	6
3.3.4	FILLER ADDITION	7
<u>4</u>	<u>NEXT STEPS</u>	<u>7</u>
4.1	PROTOTYPE ASSEMBLY	7
4.2	RHEOLOGICAL MEASUREMENTS	8
4.3	ADCB	8

1 Summary

Preparations have begun to integrate the three components of Polymer Claw into a single system. We have begun constructing low areal density abrasive brushes that will collapse under reasonable loads (~20 lbs.). Rheological measurements indicate pseudoplastic behavior in the sulfuric acid paste that will help to attain a reasonable shelf life (~ 1 wk.). The microcapsule diameter has been halved in order to improve mixing in the pressure-activated adhesive and achieve greater bond strengths at short times.

2 Project Goals and Objectives

Month 6 begins the integration of the three Polymer Claw components into a single system. For the next 4 months, we will be working towards the fabrication of full prototypes for testing. By the end of December, our final milestone is to adhere to a biofouled surface with an adhesive strength of 5 MPa under wet conditions.

3 Key Accomplishments

3.1 Abrasive Brush Fabrication

Load-displacement measurements last month showed that 200 lbs. was required to collapse an abrasive brush with a 30° bristle angle and 50% bristle density. A diver would be incapable of delivering such loads during the application of the adhesive. A force of 20 lbs. is more reasonable for the given CONOPS. If we assume a linear dependence between force and bristle density, the bristle density would have to be reduced to 5% to get a critical load of 20 lbs. Using a similar argument, abrasive brushes with a 45° bristle angle would have to be reduced to a 10% bristle density. We have therefore fabricated a pair of 30°/5% brushes and a pair of 45°/10% brushes in preparation for prototype testing next month.

3.2 Caustic Cleaning Agent Rheology

One of the requirements for the caustic cleaning agent is that it should retain its shape when not in use, but flow with little resistance when sheared. A material that does not flow below a critical stress is called a Bingham plastic. That is, the material acts like a solid below a critical stress. In comparison, a material that flows with less resistance with the increase in shear stress is called a pseudoplastic or shear thinning. These properties are illustrated in Figure 1 below (for comparison purpose, Newtonian fluid is also shown). Figure 2 shows that the current mixture of sulfuric acid, diatomaceous earth, and polyacrylic acid follows the pseudoplastic behavior. The material shear thins, but does not have a well-defined yield stress.

In the future, we would prefer a material that is both pseudoplastic and a Bingham plastic. However, in the interest of time and budget, we will limit the scope of our explorations to changes in the diatomaceous earth and polyacrylic acid concentrations. If we cannot achieve a

well-defined yield stress, we will focus on designing the caustic paste so that it retains its shape as long as possible without compromising its ability to digest cellulose.

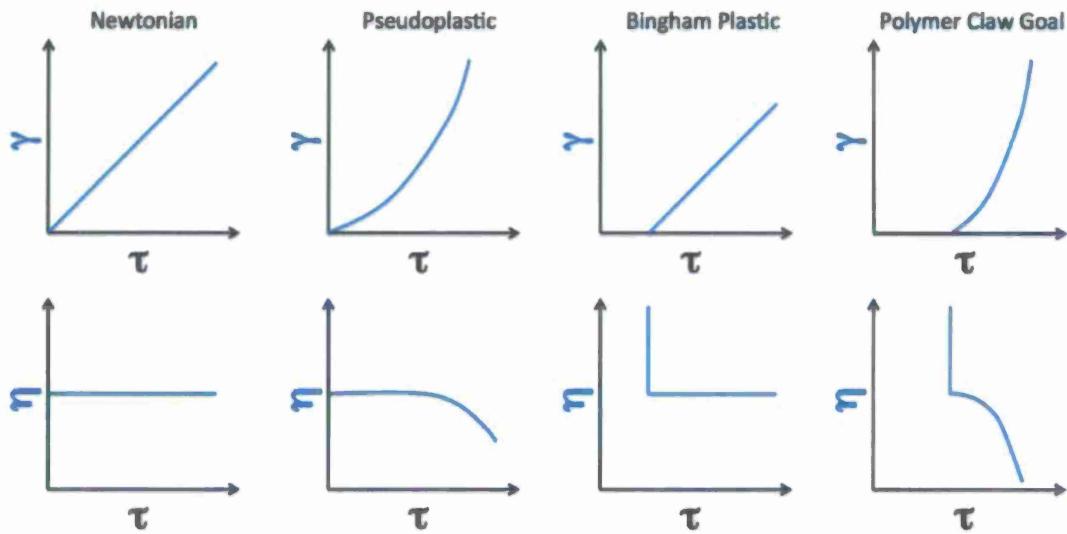


Figure 1: Illustration of shear strain (γ) and viscosity (η) versus shear stress (τ) for different types of materials. For the caustic cleaning agent, we desire a pseudoplastic with a large curvature, and a Bingham plastic with a large yield stress.

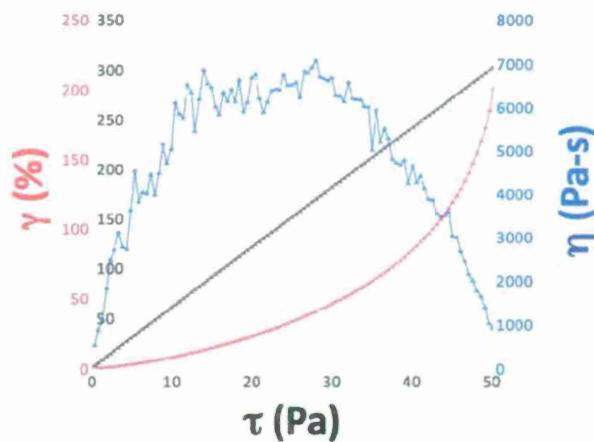


Figure 2: Plot of shear strain and viscosity versus shear stress for a sulfuric acid paste with 0.44 wt. % polyacrylic acid (PAA), and 11 wt. % diatomaceous earth (Celite). This formulation exhibits pseudoplastic behavior.

A third property that would be useful for the sulfuric acid paste is to have rheopectic properties. This rare property is common in some clay suspensions, and it refers to the ability to increase in viscosity with increasing time at a constant shear stress. A rheopectic liquid will not creep as much under the force of gravity. As shown in Figure 3, the shear rate (as shown by the slope of the blue curve) slows down over time. In the absence of a well-defined yield stress, the rheopectic behavior will reduce the dripping of the sulfuric acid paste during storage.

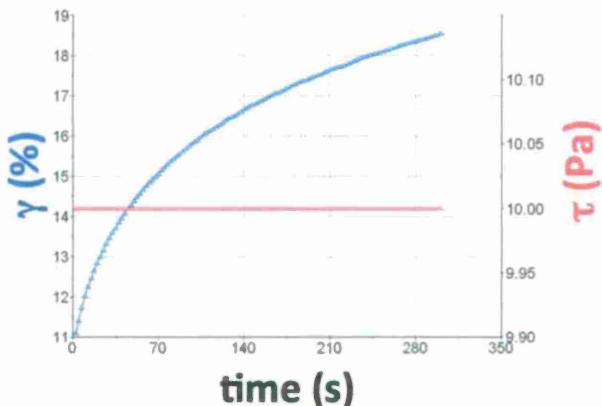


Figure 3: Plot of shear strain and shear stress versus time. Note how the slope of γ , or shear rate, is decreasing with time. Since viscosity is equal to the shear stress divided by the shear, the viscosity here is increasing with time.

3.3 Pressure-Activated Adhesive

3.3.1 Processing Improvements

In our attempts to improve the polymerization rate of the pressure-activated adhesive, we tried replacing diethylenetriamine (DETA) with ethylene diamine (ED). We observed that isophorone diisocyanate (IPDI) would precipitate from hexane that was previously exposed to ED. The cloudy appearance was actually due to the polymerization between IPDI and ED dissolved in hexane. Although ED is immiscible with hexane, the two phases are not pure ED and pure hexane. Rather the ED has some solubility in the hexane-rich phase and vice versa. This phenomenon only became noticeable because the small ED molecule has a relatively high solubility in hexane compared to the larger DETA and polyethylenimine (PEI) molecules.

This finding made it clear that higher molecular weight amines would be preferable for our synthesis. In particular, PEI would form better microcapsules because it would have virtually no solubility in hexane. It would only form a polymer with IPDI at the hexane/PEI interface. Smaller molecules such as ED would form excess polymer in the hexane phase that would not contribute to the formation of the microcapsules. More importantly, the polymerization taking place in the hexanes would reduce the stability of the microcapsules and lead to unwanted aggregation.

This unwanted aggregation explains why our previous recipe called for a slow addition of IPDI. Rapid addition of IPDI was causing uncontrolled polymerization with DETA in the hexane phase. By switching to 100% PEI as the amine crosslinker, it is now possible to add the entire batch of IPDI at once. Furthermore, switching from hexane to mineral oil as the solvent means that we no longer need polyisobutylene as a thickener. The reaction takes place more rapidly now and in much higher yield.

3.3.2 Microcapsule Diameter

One of the limitations to pressure-induced curing is the poor mixing between the amine crosslinker and isocyanate resin when the microcapsules rupture. Part of the issue is that the

microcapsules are relatively large. Extensive mixing is required after rupture because the isocyanate/microcapsule mixture is heterogeneous to begin with. The most straightforward strategy for improving mixing is to reduce the size of the microcapsules. Smaller microcapsules are more finely dispersed to begin with, reducing the burden of mixing after rupture.

The maximum speed on the mechanical mixer is 2000 RPM, and this speed yields microcapsules with a $69 \pm 16 \mu\text{m}$ average diameter. Since the mixer is being used at its maximum limit, we have switched from a paddle blade to a rotor-stator mixer. The rotor-stator creates a fine emulsion at 10 000 RPM, and then the emulsion is transferred to the mechanical mixer for the interfacial polymerization step. The results are shown in Figure 4 below: Note the improved quality of the microcapsule shape, the reduced amount of impurities on the glass slide, and the reduced diameter. The combination of the rotor-stator mixer and mechanical stirrer yielded microcapsules with an average diameter of $36 \pm 14 \mu\text{m}$. Thus the average diameter was cut in half.

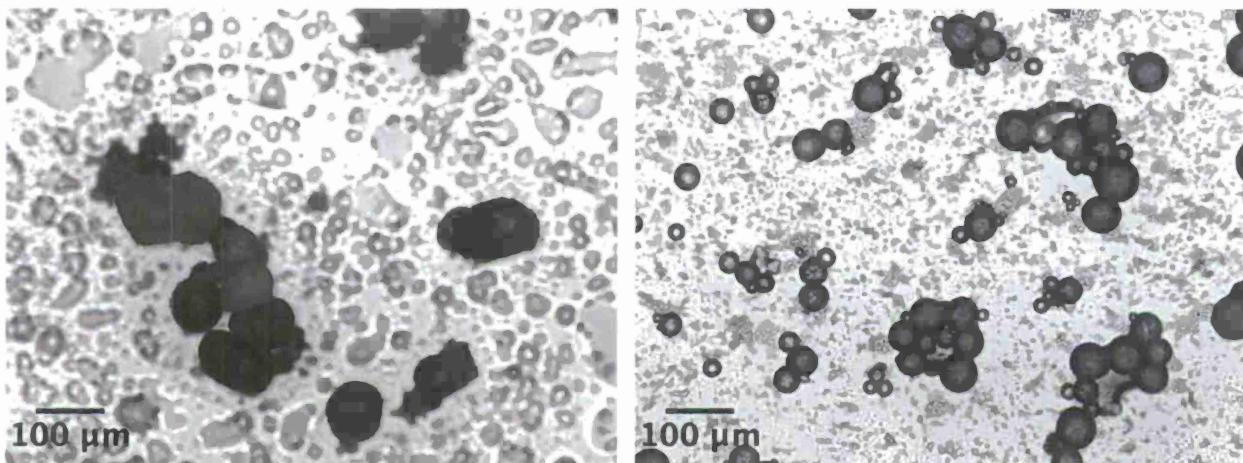


Figure 4: Comparison of microcapsules made using a mechanical mixer at 2000 RPM (left) versus microcapsules made with a rotor stator mixer at 10 000 RPM followed by mechanical mixing at 2000 RPM. The average diameter was reduced from $69 \mu\text{m}$ to $35 \mu\text{m}$.

3.3.3 Microcapsule/Resin Ratio

Asymmetric double cantilever beam (ADCB) measurements were performed on the pressure-activated adhesive. For each measurement, the adhesive was applied to a glass slide, and another glass slide was clamped down on top of the adhesive prior to testing. The time between the application of pressure and the test was 5 min for all measurements reported here.

The first optimization was to determine the ratio of microcapsules and isocyanate resin that yielded the best cure at short times. We therefore tested the following microcapsule/resin ratios: 1, 1.5, and 2. Figure 5 depicts a slight maximum for a ratio of 1.5, but further testing will be required to validate this measurement. It was clear from the sample images that the uncured resin was forming a meniscus along the crack front. ADCB is only valid for elastic beam bending. The high degree of fluid flow that is still occurring may preclude the use of short cure times. Tests performed after 30-minute cure times may therefore be preferable.

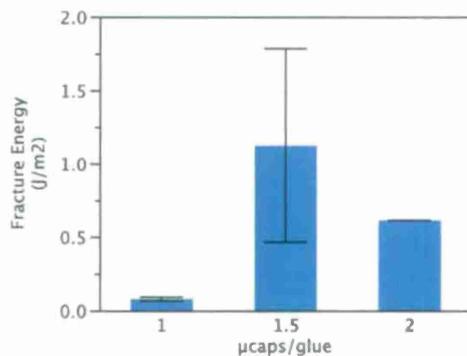


Figure 5: ADCB measurements of fracture energy after 5 min versus microcapsule to resin ratio.

3.3.4 Filler Addition

Also tested was the addition of diatomaceous earth as a filler. We hypothesized that a filler might promote microcapsule rupture and enhance the mixing of the resin with the crosslinker. In this case, we observed minimal change due to the presence of 1 wt. % Celite. 10 wt. % Celite actually resulted in a fracture energy reduction.

As in the previous section, we are unsure whether the liquid meniscus is obscuring the true result. We will therefore explore other options for improving this measurement, such as performing it at longer times.

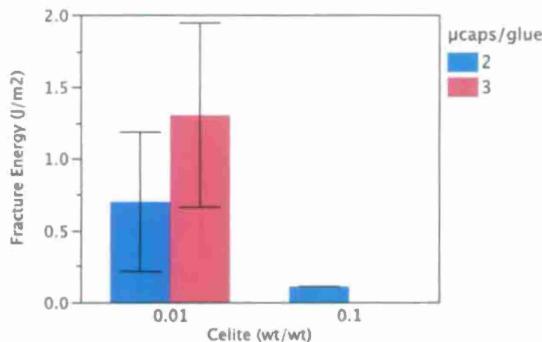


Figure 6: Plot of fracture energy versus Celite loading, grouped by the microcapsule to resin ratio.

4 Next Steps

4.1 Prototype Assembly

Rather than wait for the end of the year, we plan to begin prototype assembly earlier than scheduled in order to identify the major challenges. The full prototype will be tested underwater against a glass plate to observe the bonding mechanisms and to assess bond strength.

4.2 Rheological Measurements

Rheological characterization will be performed on all sulfuric paste formulations that were tested in month 5. By comparing the rheological properties with the cellulose breakdown data, we will choose the formulation that best satisfies the requirements for shelf life and caustic cleaning.

4.3 ADCB

The ADCB measurements will be further refined for testing adhesives that are not completely cured. The resulting data will then allow for more reliable optimization of the microcapsule loading, microcapsule size, and filler content of the pressure-activated adhesive.